(54) **SYNTHESIS OF CHEMICALLY REACTIVE CERIA COMPOSITE NANOPARTICLES AND CMP APPLICATIONS THEREOF**

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(57) **ABSTRACT**

The present invention provides a method of synthesizing nanosized abrasive particles and methods of using the same in chemical mechanical polishing slurry applications. The nanosized abrasive particles according to the invention are produced by hydrothermal synthesis. The crystallites of the particles include cerium atoms and atoms of metals other than cerium. In a preferred embodiment of the invention, the crystallites exhibit a cubic crystal lattice structure. The differences in electric potential between the cerium atoms and the atoms of metals other than cerium facilitate the polishing of films without the need for chemical oxidizers.

Sample No.	Guest Metal (M)	Mole Ratio Ce:M	Polish rate A/min	Oxidation State	Ionic radius, A	Primary particle size, nm	Secondary particle size, nm	Zeta potential, mV
1	Ti	4:1	4300	4	0.68	15	697	76
2	Ta	4:1	4000	5	0.70	8.42	102	5.66
3	Y	4:1	3830	3	0.93	9.47	2100	151.38
4	Mn	4:1	3530	4	0.54	11	186	36.81
5	In	4:1	3180	3	0.81	12	2631	-16.68
6	Sb	4:1	2420	3	0.90	6.3	121	14.34
7	Cd	4:1	2160	2	0.97	6.32	268.1	9.92
8	Zn	4:1	1690	2	0.74	4	287	88.42
9	Cu	4:1	1680	2	0.72	7.4	142	23.56
10	Fe	4:1	1600	3	0.64	10	284	-16.68
11	Sn	4:1	1480	4	0.71	15.7	53.2	38.5
12	Si	4:1	1280	4	0.41	6.32	2175	82.7
13	Se	4:1	416	4	0.69	26.4	133	32.09
14	Ni	4:1	302	2	0.72	7.89	895	79.03
15	W	4:1	299	6	0.65	4.21	496	-44.01
16	Co	4:1	266	3	0.63	12.5	113	34.8
17	Sr	4:1	193	2	1.13	6.31	91	3.95
18	Mg	4:1	184	2	0.65	6.32	148	23.15
19	Cr	4:1	89.2	3	0.64	13	125	3.34
20	La	4:1	88.7	3	1.06	6.32	884	57.27
21	Pr	4:1	64.1	4	0.90	7.78	178	34.58
22	Nd	4:1	55	3	1.00	6.3	212	27.95
23	Ba	4:1	39.6	2	1.35	7	139	9.28
24	Al	4:1	21.4	3	0.50	9	2174	278.43
25	Tl	4:1	3.44	3	0.95	6.3	115	25.86
26	Nb	4:1	0.382	4	0.74	8.5	58	-17.38
27	Ca	4:1	0	2	0.99	6.5	134	7.89
28	Zr	4:1	0	4	0.79	8.42	1316	138.92
29	Sm	4:1	0	3	0.96	7.78	165	29.33
30	Gd	4:1	0	3	0.94	6	352	34.9
31	Eu	4:1	0	3	0.95	5.26	269	39.36
32	Hf	4:1	0	4	0.78	5.26	127	30.1
33	Bi	4:1	0	3	0.96	5	191	42.47
34	None	N/A	3.14	4	0.92	6	27	29.13

Figure 1

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RELATED APPLICATIONS

[0001] This application is a continuation-in-part of co-pending Appn. Ser. No. 10/255,136, filed Sep. 25, 2002, which is a continuation in part of Appn. Ser. No. 09/992,485, filed Nov. 16, 2001, now U.S. Pat. No. 6,596,042.

FIELD OF THE INVENTION

[0002] The present invention provides a process for producing abrasive particles, the abrasive particles produced according to the process, and a process for removing a film layer using a CMP slurry containing particles made by the process.

BACKGROUND OF THE INVENTION

[0003] Chemical-mechanical polishing (CMP) slurries are used, for example, to planarize surfaces during the fabrication of semiconductor chips and related electronic components. CMP slurries typically include reactive chemical agents and abrasive particles dispersed in a liquid carrier. The abrasive particles perform a grinding function when pressed against the surface being polished using a polishing pad, and separately, the reactive chemical agents serve to oxidize the surface.

[0004] It is well known that the size, composition, and morphology of the abrasive particles used in a CMP slurry can have a profound effect on the polishing rate and surface finishing. Over the years, CMP slurries have been formulated using abrasive particles formed using, for example, alumina (Al_2O_3), cerium oxide, or ceria (CeO_2), iron oxide (Fe_2O_3), silica (SiO_2), silicon carbide (SiC), silicon nitride (Si_3N_4), tin oxide (SnO_2), titania (TiO_2), titanium carbide (TiC), tungsten oxide (WO_3), yttria (Y_2O_3), zirconia (ZrO_2), and combinations thereof.

[0005] Known abrasive particles for use in CMP slurries include colloidal silica, which is produced by condensation in aqueous solution. Another is fumed silica, which may be produced by a continuous flame hydrolysis technique involving the conversion of silicon tetrachloride ($SiCl_4$) to the gas phase using an oxy-hydrogen flame. The silicon tetrachloride reacts with the combustion by-produce (water) to yield silica (SiO_2) and hydrochloric acid: $SiCl_4+2H_2O \rightarrow SiO_2+4HCl$. The HCl is easily separated as it remains in the gas phase, while the fumed silica is solid. In order to attain a desired particle size, the fumed silica is mechanically ground or milled. Fumed silica is by far the most widely used abrasive particle.

[0006] Calcination is another method of producing abrasive particles for use in CMP slurries. During the calcination process, precursors such as carbonates, oxalates, nitrates, and sulfates, are converted into their corresponding oxides at very high temperature. After the calcination process is complete, the resulting oxides must be milled to obtain particle sizes and distributions that are proper to provide desired removal rate and prevent scratching.

[0007] The calcination process, although widely used, does present certain disadvantages. For example, it tends to be energy intensive and can produce toxic and/or corrosive gaseous byproducts. In addition, contaminants are easily introduced during the calcination and subsequent milling processes. Finally, it is difficult to obtain a narrow particle size distribution.

[0008] The basic mechanism of the CMP process is the simultaneous formation of a removable surface layer, such as via oxidation of a metal surface or via hydrolysis of an oxide or nitride layer, coupled with the mechanical removal of the removable surface layer using abrasive particles pressed between the work piece and a polishing polishing pad that are in motion relative to each other. In CMP slurries for removing copper films, the mechanical (abrasive) effect and oxidizing function are separately provided by the different components. That is, abrasive particles mainly contribute the mechanical effect, while chemical oxidizing agents give rise to a chemical (redox) reaction.

[0009] Numerous chemical additives exist to improve film removal rates, to adjust the selectivity of removal rates between various materials, and to allow better surface finishing and less defects. Hydrogen peroxide, ferric nitrate, potassium iodate and periodate are widely used as oxidizing chemicals in copper CMP slurries to improve removal rates relative to slurries having only abrasive particles. Most CMP slurries are formed by combining two separate components, namely: (1) abrasive particles dispersed in a liquid medium; and (2) chemical additives (e.g., a chemical oxidizer). The separate components are mixed together immediately prior to use and, once blended, have a shelf life of typically only about 5 days or less. The chemical oxidizer in conventional CMP slurries tends to lose its oxidative efficacy if it remains unused for long periods.

[0010] While the use of chemical oxidizers improves the metal removal rate to industrially practicable levels, the chemical oxidizers in the slurry continue to oxidize metal until they are expended or removed. Hence, chemical oxidizers are one of main contributors to the problem of dishing or pitting of metal surfaces, which results from continued oxidative attack on an already planar metal surface, even in the absence of abrasive particles.

BRIEF SUMMARY OF THE INVENTION

[0011] Broadly, the abrasive particles according to the invention comprise crystallites (primary particles) that include cations of cerium and cations of at least one other metal, which have been formed by hydrothermal synthesis. The abrasive particles can be used to formulate CMP slurries that provide industrially acceptable removal rates of a variety of surface films (substrates), without the need for added chemical oxidizers, which eliminates concerns about dishing and cupping. Slurries formulated using abrasive particles according to the invention exhibit a shelf life far greater than traditional CMP slurries. Another advantage provided by the abrasive particles according to the invention is that use of chemical oxidizers can be avoided, which reduces the environmental impact of producing electronic components.

[0012] The foregoing and other features of the invention are hereinafter more fully described and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the various ways in which the principles of the present invention may be employed.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] **FIG. 1** is a Table displaying several properties and polishing rates of the abrasive particles formulated in Example 5.

DETAILED DESCRIPTION OF THE INVENTION

[0014] The invention provides a method of synthesizing abrasive particles having a desired reactivity, which can be used in formulating CMP slurries exhibiting a variety of substrate removal rates. The inventive particles may be used to polish metal substrates or metal oxide substrates. Both operations are routinely required in the manufacture of electronic components. The substrate removal rate of CMP slurries is believed to depend on numerous factors. A non-exhaustive list of such factors includes: the composition of the abrasive particles; the relative level and identity of guest metal ions in those particles; the size of the primary particles (i.e., crystallite size); the size of secondary particles (i.e., coalesced or agglomerated primary particles); the concentration of abrasive particles in the slurry; the pH of the slurry; and the presence and concentration of chemical oxidizers in the slurry. The focus of the present invention is the control of primary and secondary particle size of the abrasive particles, and the control of the level of guest ions in such primary particles. Chemically reactive abrasive particles according to the invention can be used in the CMP process to produce both chemical and mechanical effects.

[0015] It has been discovered that nanoscale composite ceria particles can be synthesized hydrothermally such that cerium oxide acts as a host matrix (crystal lattice structure) for guest metal atoms (or ions) that take the place of cerium atoms (or ions) in the crystal lattice structure of the host matrix. The inventive process produces "nanoscale" particles, with primary particles (crystallites) having a mean diameter (D_{50}) in the range of about 1 nm to about 10000 nm. In a preferred embodiment, the average crystallite size may be about 5 to about 1000 nm, more preferably about 10 to about 400 nm, still more preferably about 15 to about 200 nm, and even more preferably about 20 to about 100 nm. Secondary particles, which are agglomerations of primary particles, exhibit sizes within the range of from about 10 to about 10000 nm, but are preferably 30 nm to about 1000 nm, more preferably from about 40 to about 800 nm and still more preferably from about 50 to about 500 nm. Throughout the instant specification and in the appended claims, the term "particle" when used without further explanation refers to secondary particles.

[0016] Generally, guest metal ions are substituted for a cerium ions in the crystal lattice structure, thus preserving the ratio of metal cations to oxygen ions in such crystal. Thus, for cerium oxide, the mole ratio of metal atoms (or cations) to oxygen atoms in the crystal lattice structure will be about 1:2, although mole ratios of metal atoms to oxygen atoms of about 1:1.5 to 1:3.5 are possible. The ratio of cerium atoms to oxygen atoms in the crystal is sufficient to preserve overall statistical electroneutrality. The resultant composite metal oxide formula is thus $Ce_xM_yO_z$ where x+y is about 1 and z is within the range of from about 1.5 to about 3.5. Because the guest metal ions (1) may have a different oxidation state than cerium and/or (2) do have a different electronegativity than cerium, the difference in electrical potential is generally sufficient to drive a redox reaction on the surface of a film to be polished when the abrasive particles according to the invention are in contact therewith. Films or substrates that can be polished (removed) using abrasive particles according to the invention include metals, metal oxides, metal nitrides, silicides, and polymers.

[0017] In particular, the invention provides a method of producing abrasive particles for use in CMP slurries comprising providing an aqueous reaction mixture comprising a source of cerium ions and a source of metal ions other than cerium. The metal ions other than cerium are selected from the group consisting of Be, B, Mg, Al, Si, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Ga, Ge, As, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Ba, La, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Hp, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi and combinations thereof. The aqueous reaction mixture is subjected to hydrothermal treatment at a temperature of from about 70° C. to about 500° C. to produce the abrasive particles. When the mole percentage of cerium atoms in the crystal lattice structure of the crystallites exceeds the mole percentage of guest metal ions, the crystallites will generally exhibit a cubic crystal lattice structure wherein cerium serves as a host cation and the metal other than cerium serves as a guest cation. When the mole percentage of cerium atoms in the crystal lattice structure is less than the mole percentage of guest metal ions, the crystallites will generally exhibit a crystal lattice structure determined by the guest metal ions, with the cerium cation serving as guests therein. The inventive abrasive particles can be dispersed in water to form CMP slurries. If desired, a pH adjuster may be added to adjust the pH to about 3 to about 11.

[0018] The precise stoichiometry used in hydrothermal synthesis dictates the final aggregate ratio of guest to host ions in the crystal structures of a sample of the inventive composite particles. An analysis of an aqueous dispersion of composite abrasive particle formed in accordance with the invention that included cerium as a host cation and titanium as a guest ion showed that the dispersion consisted mainly of small particles having a particle size distribution in the range of 6 to 30 nm, along with a few larger particles having a size of about 160 nm. The smaller particles exhibited a spherical shape, whereas the larger particles appeared to be more rectangular. The EDS spectrum for the large particles showed that they consist of 95 wt % ceria and 5 wt % titania, while the smaller particles consist of 58 wt % ceria and 42 wt % titania. Thus, it will be appreciated that variations in the relative mole percentage of cerium ions to guest ions will occur in individual particles, which may be different than the average relative mole percentage for the bulk of the particles. In other words, while the aggregate composition of a dispersion of inventive particles will have a makeup approximately the same as the relative amounts of reagents used, the composition of a single given particle, or any subset of particles from such a dispersion may have a composition widely different from the aggregate.

[0019] In the aggregate, the mole ratio of cerium ions to guest ions in abrasive particles according to the invention will be from about 100000:1 to about 1:100000. In order to retain the desired cubic crystal lattice structure of cerium oxide, the mole ratio of cerium ions to guest ions in the abrasive particles according to the invention will be within the range of from about 1000:1 to about 1:1. Still more

preferably, the aggregate mole ratio will be within the range of from about 90:1 to about 1.5:1. It will be appreciated that as the concentration of guest ions increases, additional crystalline phases tend to appear in the primary particles. For example, crystallites containing substantial molar quantities of ceria and titania will exhibit both a cubic crystalline phase and an anatase crystalline phase, although both crystals contain ions of both cerium and titanium.

[0020] The cerium host ions may be provided by a Ce(III) salt or a Ce(IV) salt, for example $Ce(NH_4)_2(NO_3)_6$. The hydrothermal treatment may be carried out for about 10 minutes to about 48 hours, preferably about 15 minutes to about 24 hours and more preferably about 1 hour to 8 hours. It is believed that the method of mixing the aqueous reaction mixture and a base has an effect on primary and secondary particle sizes. For example, blending a base into the aqueous reaction mixture by double jet injection is effective in synthesizing composite ceria particles having desired small crystallite sizes. Ceria particles having crystallite sizes of about 10 nm to about 100 nm provide superior polishing rates in CMP operations.

[0021] The reaction mixture may be heated to a temperature of about 70° C. to about 500° C., or to a temperature of about 200° C. to about 400° C. Preferably the second reaction mixture is heated to a temperature of about 300° C.

[0022] The source of guest ions is not critical. Accordingly, the source of guest metal ions may be a salt of the guest ion. The guest ion salt may be selected from the group consisting of nitrates, chlorides, perchlorides, bromides, sulfates, phosphates, carbonates, and acetates of the guest ion. Metal ethoxides may also be used. In a preferred embodiment, the source of guest ions may be $Fe(NO_3)_3$, $Cu(NO_3)_2$, $Nd(NO_3)_3$, or the hydrated forms thereof.

[0023] These composite particles can be used as chemically reactive abrasives in CMP slurries to remove metal film layers such as copper without the need for added oxidizers. Metal oxides, nitrides, silicides and polymers may also be polished effectively. Metals that can be polished by the inventive methods include silver, gold, platinum, copper, palladium, nickel, cobalt, iron, ruthenium, iridium, and osmium, silicon, aluminum, germanium, tungsten, tantalum and alloys or blends thereof.

[0024] Metal oxides that can be polished by the inventive methods include oxides of metals such as boron, sodium, magnesium, aluminum, silicon, phosphorus, potassium, calcium, gallium, germanium, arsenic, selenium, rubidium, strontium, yttrium, zirconium, tin, antimony, cesium, and barium. Metal oxide substrates may also contain more than one of the aforementioned oxides. Metal nitrides can also be polished.

[0025] Low K-value dielectric materials may also be polished. Many of these are polymeric, for example poly-para-xylenes commercially available from S. C. Cookson, of Indianapolis, Ind., under the Parylene tradename. Further such polymers include fluorinated polyimides, methyl silsesqioxane, and poly-(arylene ether)s. The Dow Chemical Company, of Midland, Mich., commercially supplies B-staged polymers including those sold by under the Cyclotene® and SiLK® trademarks. For example, Cyclotene® 4026-46 is a blend of B-staged divinylsiloxane-bis-benzo-cyclobutene, mesitylene, polymerized 1,2-dihydro-2,2,4-tri-

methylquinoline, 2,6-bis{(4-azidophenyl) methylene}-4-ethylcyclohexanone, and 1-1'-(1-methylethylidene) bis {4-(4-azidophenoxy)benzene}. In general, the Cyclotene® dielectric polymers contain at least B-staged divinylsiloxane-bis-benzocyclobutene and mesitylene. Polymers sold under the SiLK® trademark are semiconductor dielectric resins comprise a Dow proprietary b-staged polymer, cyclohexanone, and gamma-butyrolactone. In addition, carbon doped silica substrates, which are also known as SiCOH substrates, can be polished.

[0026] The difference in valence state and/or electronegativity between ceria and the guest ions in the abrasive particles according to the invention gives the particles the ability to provide the redox potential to films to be removed. Hence, it is believed that such oxidation occurs only when a particle contacts the substrate surface, and consequently, that oxidation and mechanical abrasion occur simultaneously. This fact, combined with the small particle size disclosed herein (nanoscale) provides extremely precise polishing, and planarization that is both locally and globally accurate. Thus, the invention further provides a method of removing a film by CMP at a desired rate in the absence of chemical oxidizers.

[0027] When all other polishing conditions are kept similar, adjustments in the relative molar percentage of guest metal ions in the crystal lattice structure of the abrasive particles according to the invention can be used to determine or tune the rate of film removal. Thus, the invention facilitates determining the rate of removal of a film layer by selecting the composition of the abrasive, rather than adjusting other polishing parameters.

[0028] The invention further provides a method of removing a portion of a substrate by contacting the substrate with a CMP slurry comprising composite abrasive particles wherein the abrasive particles comprise cerium ions and guest metal ions selected from the group consisting of iron, copper, neodymium, and combinations thereof, and wherein the slurry contains no additional oxidizers.

[0029] The invention also provides a method of producing a CMP slurry comprising contacting the particles discussed hereinabove with water to form a suspension and adjusting the pH of the suspension to about 2.0 to about 11.0 with a pH adjuster, wherein the slurry is substantially free of chemical additives and oxidizers.

[0030] Because the particles of the present invention are so small, i.e., primary particle diameters on the order of nanometers, a very high fraction of the atoms reside at the particle crystalline surfaces and grain boundaries. As primary particle size decreases, the BET specific surface area (m^2/gram) increases. Without being limited to any theory, applicants postulate that nanoparticles are much more reactive than the corresponding bulk material due to vastly increased specific surface area. It is further believed that surface defects, non-balanced charges, guest ions in the grain boundary and vacancies in the crystalline lattice and other surface active sites may beneficially induce or catalyze chemical redox reactions.

[0031] Hydrothermal synthesis of cerium oxide abrasive particles is disclosed in commonly owned U.S. Pat. No. 6,596,042, which is hereby incorporated by reference. In order for the particles to function as chemically active

nanoparticles, the nanoparticles must be able to form a stable suspension in water. In developing the embodiments of the present invention, hydrothermal synthesis of ceria was carried out in order to facilitate crystallization of the desired abrasive oxide particles containing guest cations.

[0032] With respect to the present invention, hydrothermal synthesis is conducted in a sealed (i.e., air-tight) container, typically made of stainless steel. A metal salt containing the host cation ingredient, i.e., cerium ions, is solubilized in deionized water. A crystallization promoter is added, and optionally, a stabilizer for the crystallization promoter is also added. The pH of the inherently acidic salt solution is raised to at least 1.5, preferably to at least 7.5, and more preferably to at least 9.0 using a base, (which may be provided in the form of a solution), which assists in the formation of a solution having a gel-like consistency. Suitable bases include, for example, NaOH, KOH, NH_4OH, organoamines such as urea, ethylamine and ethanolamine, and/or polyorganoamines such as polyethylenimine. Combinations of bases can also be used. Other compounds such as urea can also be added to assist in crystal growth. The gel-like solution will break down into small particles upon rapid stirring. Double injection mixing can be used to ensure stoichiometric homogenization of the metal salt solutions with the base(s) to ensure uniform crystal seed generation. Hydrothermal synthesis is carried out in a closed container because the pressure generated by the raised temperature results in small particles having a narrow size distribution resulting from uniform crystal growth. The solution may be further diluted with deionized water as needed. The solution is transferred to a sealed stainless steel reaction vessel, which is heated to 70-500° C. for about 1 hour to about 500 hours under stirring. The vessel is then cooled to room temperature, and the slurry is washed until a low conductivity is achieved, typically <5 mS, preferably <1 mS, more preferably <0.5 mS and most preferably <0.1 mS. As a final purifying step, the particles may be filtered using micron range filter paper.

[0033] Crystallization promoters include titanium chloride, titanium sulfate, titanium bromide, organotitanium compounds such as titanium oxychloride and those sold by E.I. DuPont de Nemours of Wilmington, Del., under the Tyzor® trademark, for example Tyzor®-TE. A preferred crystallization promoter is $Ti[OCH(CH_3)_2)]_4$ (titanium (IV) isopropoxide). It will be appreciated that certain titanium compounds tend to rapidly decompose in aqueous media, which reduces their efficiency in promoting the formation of particles having larger crystallite sizes. Accordingly, it is preferable for one or more stabilizing compounds such as, for example, acetyl acetone, (i.e., acetyl acetone titanate) to be present with the crystallization promoters in order to prevent or delay their decomposition. Further details on crystallization promoters and stabilizers can be found in commonly owned U.S. Pat. No. 6,596,042, and copending application Ser. No. 09/992,485. The guest ions are incorporated into the cerium oxide crystal structure without disrupting the cubic structure thereof.

[0034] Although the preceding description and following experimental examples will show that the inventive abrasive particles alone—absent oxidizers and other chemical additives—can be used to exhibit a wide variety of satisfactory metal removal rates on a copper substrate, the metal removal rates of any inventive particle can be further adjusted by the

use of chemical additives, including oxidizers. Such chemical additives include hydrogen peroxide, ascorbic acid, citric acid, formic acid, acetic acid, propionic acid, butyric acid, valeric acid, acrylic acid, lactic acid, succinic acid, nicotinic acid, oxalic acid, malonic acid, tartaric acid, malic acid, glutaric acid, citric acid, maleic acid, and glycine.

[0035] The following examples are intended only to illustrate the invention and should not be construed as imposing limitations upon the claims. The following experimental methods, conditions and instruments were employed in preparing the exemplary CMP particles detailed hereinbelow.

EXAMPLE 1

[0036] An abrasive particle suitable for CMP was prepared by first dissolving 1854 g (3.38 mol) of $Ce(NH_4)_2(NO_3)_6$ in 3500 g of deionized water. To this solution, 100 g of Ti(isopropoxide)4 (0.35 mol) and 90 g of acetyl acetone was added. The cerium salt solution was mixed with a basic solution (containing 1000 g H_2O and 1043 g of KOH) using a controlled double jet injection method with constant stirring. The slurry thus formed was diluted to a volume of 8330 mL with deionized water, and heated in a sealed stainless steel vessel, i.e., a hydrothermal reactor, at 300° C. for 6 hours with agitation. After the slurry was discharged from the hydrothermal reactor, the slurry was decanted several times before being subjected to cross-flow washing until a conductivity of 0.075 mS was achieved. The slurry was then subjected to a Dual-Frequency Reactor (Advanced Sonic Processing Systems) for sonification at a flow rate of about 50 ml/minute. The resultant final CeO_2 particles exhibited a primary particle size of about 17 nm and a secondary particle size of about 800 nm. A slurry of 1 wt % CeO_2 particles was prepared in water adjusted to a pH of 4 with HNO_3). This slurry was used for copper CMP on a Strasbaugh 6EC polisher with 3/1 psi & 60/60 rpm and with a slurry flow rate of 170 ml/min. A Cu removal rate of 1004 Å/min was obtained. The particle distribution was (d10) 50 nm, (d50) 120 nm, and (d90) 400 nm, and the particles exhibited a crystallite size of 17 nm.

EXAMPLE 2

[0037] In a 500 ml beaker, 85.16 g of cerium ammonium nitrate $Ce(NH_4)_2(NO_3)_6$ was dissolved in 300 ml deionized water, and 6.34 grams (0.0157 mol) of ferric nitrate nonahydrate $(Fe(NO_3)_3.9H_2O)$ was added with stirring. The solution was diluted further by addition of 350 ml of deionized water. A basic solution was formed by dissolving 48.72 grams of potassium hydroxide (KOH) in 350 ml deionized water. The solutions (1) containing cerium ammonium nitrate and ferric nitrate and (2) the base were simultaneously introduced under stirring into a 1000 ml beaker via a controlled double jet injection method. After the solutions were added together, the resulting solution was stirred for 5 minutes and then ultrasonicated for 15 min. The solution was transferred to a sealed 1000 ml stainless steel reaction cylinder, and then placed in a preheated oven at 300° C. for 4 hours. The reaction cylinder was removed from the oven, cooled to room temperature, and the contents were transferred to a 1000 mL plastic container. The reaction product consisted of a dispersion of cerium oxide-ferric oxide composite nanoparticles. The product slurry was then washed to remove excess unreacted ionic salts. The disper-

sion was ultrasonicated for 15 minutes and then filtered to afford a final product with pH 4±0.5 and conductivity less than 0.07 mS. The final product was filtered through 12-micron filter to remove possible external impurities. The Cu CMP slurry was made by diluting the above particles to a 1 wt % dispersion using deionized water adjusted to a pH of 4 using nitric acid (HNO_3). The Cu CMP operation of Example 1 was performed using the composite Ce—Fe particles this formed. A Cu removal rate of 1762 Å/min was obtained. This indicates that the Ce—Fe composite particle is chemically more active than the pure CeO_2 nanoparticles used in the comparative example. The particle distribution is (d10) 88 nm, (d50) 143 nm, and (d90) 346 nm, and the particles exhibited a crystallite size of 10 nm.

EXAMPLE 3

[0038] A dispersion of cerium oxide-copper oxide composite nanoparticles was formed using the same materials and procedure set forth in Example 1, except that 13.36 g of copper nitrate hemipentahydrate ($Cu(NO_3)_2.2.5H_2O$) was used instead of ferric nitrate nonahydrate. The Cu CMP was performed under the same conditions as in Example 1. A Cu removal rate of 2021 Å/min was obtained, indicating that Ce—Cu composite nanoparticles are chemically more active than pure CeO_2 particles. The particle distribution is (d10) 158 nm, (d50) 316 nm, and (d90) 747 nm, with a crystallite size of 7.4 nm.

EXAMPLE 4

[0039] A dispersion of cerium oxide-neodymium oxide composite nanoparticle dispersion was formed using the same materials and procedure set forth in Example 1, except that 11.85 grams of neodymium (III) nitrate hexahydrate ($Nd(NO_3)_3.6H_2O$) was used instead of ferric nitrate nonahydrate. The Cu CMP was performed under the same conditions as in Example 1. A Cu removal rate of 1980 Å/min was obtained, indicating that Ce—Nd composite nanoparticles are chemically more active than pure CeO2 nanoparticles. The particle distribution is (d10) 89 nm, (d50) 157 nm, and (d90) 437 nm and the particles exhibited a crystallite size of 6.3 nm.

EXAMPLE 5

[0040] Composite cerium oxide particles were made in the following manner. Except for the identity and amount of guest reagent added, the syntheses were substantially identical. In a 1000 ml beaker, 80.2 g (0.146 moles) of cerium ammonium nitrate $Ce(NH_4)_2(NO_3)_6$ was dissolved in 200 ml deionized water to form a well mixed aqueous solution of cerium salt. To the solution 18.95 g (0.036 moles) of acetyl acetone titanate was added. The salt solution was well mixed until it was clear and homogeneous. A sufficient quantity of DI-water was then added to reach a final volume of 300 ml. In another 1000 ml plastic bottle, 48.7 g (0.338 moles) of potassium hydroxide (KOH) was added to DI water and diluted to a final volume of 300 ml. Using a controlled double jet injection the salt solution and the base solution are mixed together with continuous agitation, and mixed an additional 5 minutes. The slurry is then ultrasonicated for 15 minutes. The slurry is then transferred to a stainless steel reaction vessel and placed in a preheated oven at 300° C. for 4 hours. The stainless steel reaction vessel is removed from the furnace and allowed to cool to room temperature. The reaction product (a dispersion of cerium oxide-titanium oxide particles) is then transferred to a clean

1000 ml container. The dispersion was washed with DI water several times to remove excess ions and to achieve subsequent separation from supernatants by settling. This was carried out several times until the ion concentration was very low (conductivity of 0.07 mS). The final product was filtered through a 12-micron filter to remove any possible external impurities.

[0041] FIG. 1 is a Table showing the molar amounts of guest ion reagents that were mixed with $Ce(NH_4)_2(NO_3)_6$ to produce the composite particles in accordance with the invention. Sample 1 is the particle made by the exemplary synthesis of Example 5. The table further displays several properties of the composite particles. The secondary particle size distribution of the composite abrasive particles was determined by a light scattering technique as known in the art, using a Horiba LA-910 particle size analyzer. The secondary particle size is defined as the size of agglomerates of primary particles.

[0042] The slurry was adjusted to a pH of 4 and the solid content adjusted to 1% before use in CMP. The particles have the polishing rate in angstroms per minute as set forth in FIG. 1. Polishing experiments were performed using Westech 372 polisher using six-inch silicon oxide wafers. An IC-1000/Suba-IV polishing pad was used for polishing. The downward pressure on the carrier was set at 3.5 psi. The back pressure on the wafer carrier was 0 psi. The carrier was rotated at speed of 93 rpm while the pad was rotated at 87 rpm. The slurry feed rate to the wafer-pad area was 150 ml. The slurries used for the study are maintained at room temperature (25° C.). The films studied were PECVD TEOS silicon dioxide on 150 mm diameter silicon wafer. The film thickness, before and after CMP, was measured optically using a Prometrics FT-750.

[0043] It is noted that sample 34 in Table 1 is a comparative example, inasmuch as it is a pure cerium oxide particle. Lacking guest metal ions, the cerium oxide particle of sample 34 exhibits a polishing rate on a silicon dioxide substrate of 3.14 Å/min.

EXAMPLE 6

[0044] To study the STI polishing performance of abrasive particles with different mole percentages of titanium ions in the crystal structure, 11 samples of abrasive particles were synthesized using the procedures and reagents described in Example 5 above to produce particles having the mole percentages of ceria and/or titania shown in Table 1 below:

TABLE 1

Sample	Ce/Ti (mole %)	Raw D_{50}	Raw Dmean (nm)
6-1	100/0	78	426
6-2	90/10	473	504
6-3	80/20	249	247
6-4	70/30	561	677
6-5	60/40	714	719
6-6	50/50	918	918
6-7	40/60	799	803
6-8	30/70	852	854
6-9	20/80	67	79
6-10	10/90	67	70
6-11	0/100	69	71

[0045] The particles were dispersed in water at a weight percent loading of 1%. HNO_3 was added to adjust the pH of the slurries to 4.0. No chemical oxidizers and/or surfactants

were added to the slurries, and the slurries were not sonicated or filtered after formation.

[0046] Samples 6-1 through 6-11 were used separately to polish 6-inch blanket thermal oxide (TOX) and nitride (NIT) wafers using a Westech 372 polisher, an IC-1000/Suba-IV pad, with a downward pressure of 3.5 psi (no back pressure), a carrier/pad rotation speed of 93/87 rpm, and a slurry feed rate of 150 ml/min. Polishing was conducted using the slurries first on a dummy silicon wafer, then on a used TOX wafer, then on a new TOX wafer and finally on a new NIT wafer. Distilled water was used to clean the wafers, which were air-dried. Polishing results are shown in Table 2 below, where "WIWNU" means WIthin Wafer Non-Uniformity:

[0049] The primary particle size increased in relation to the increases in titanium ions present, with the lattice constant decreasing from 5.42 Å for pure ceria to 3.81 Å for pure titania. The lattice constant remained similar to pure ceria until the mole percentage of titanium ions reached about 50 mole %. After that point, the crystal structure of the ceria-titania composite abrasive particles became more similar titania, which means that cerium ions were guest ions and titanium ions were the host ions in the crystal structure, which was anatase. Particles of this type were not as good for oxide polishing as particles that exhibited a substantially cubic crystal structure.

TABLE 2

	Polish rate (nm/min)		Polish rate (nm/min)		Polish rate (nm/min)			Surface	TOX/NIT
Sample	TOX Used	WIWNU	TOX2 New	WIWNU	Avg TOX	NIT	WIWNU	Rough (nm)	Selectivity
6-1	4.1	35.53%	−1.2	37.60%	1.45	0.5	47.59%	1–1.5	2.9
6-2	339.1	24.04%	261.9	26.48%	300.5	197.9	6.38%	1–1.2	1.518444
6-3	43.6	34.53%	36.3	36.04%	39.95	224.3	7.09%	1.1–1.5	0.17811
6-4	399.5	15.45%	232.5	15.80%	316	234.6	5.10%	0.9–1.5	1.346974
6-5	335.9	11.74%	352.5	9.72%	344.2	159.2	5.05%	1.7–1.9	2.16206
6-6	300.1	12.32%	260.4	13.50%	280.25	18.3	36.33%	0.8–2.0	15.31421
6-7	196.4	16.85%	168.3	16.74%	182.35	2.7	33.11%	2.1–3	67.53704
6-8	260.6	9.40%	251.9	11.98%	256.25	96.3	6.50%	1.1–1.4	2.660955
6-9	90.9	16.29%	110.8	17.83%	100.85	2.7	37.34%	1.4–1.9	37.35185
6-10	N/A	N/A	4.6	29.61%	4.6	28.9	22.32%	1.2–1.5	0.15917
6-11	N/A	N/A	19.7	29.09%	19.7	23.3	26.34%	1.1–1.2	0.845494

[0047] The results shown in Table 2 above show that pure ceria particles (i.e., containing no titanium ions) did not polish TOX or NIT wafers at a very high rate. The removal rate increased as titanium ions were introduced into the ceria crystal structure, and then decreased as the concentration of titanium ions reached about 70 mole percent. In the case of pure titania, both TOX and NIT removal rates were very low due to the inherent properties of titania particles.

[0048] The TOX wafer surface for the slurries containing between 50 mole % and 80 mole % titanium ions are very rough due to the large secondary particle sizes and the presence of needle-like particles, which lead to some scratches on the wafers. In the case of 70 mole % titanium ions, a better result may be attributable to a comparatively small after formulation secondary particle size (Dmean=338 nm vs. 404-1188 nm). In the range of 10 mole % to 40 mole % titanium ions, the TOX polishing rate is high and the nitride removal rate is ideally not very high. The results for Sample 6-3 (i.e., the 20 mole % titanium ions sample) are questionable and may not be reliable.

EXAMPLE 7

[0050] Abrasive particles were formed in accordance with the procedures and using the reagents and equipment as described in Example 5, except that the mole percentage of titanium cations to cerium cations was 5.95% (Ti) to 94.05% (Ce). The raw mean particle size (D_{50}) of the abrasive particles was 79 nm. The abrasive particles were dispersed at different loadings in water to form slurries. No chemical oxidizers or surfactants were added, and the slurries were not sonicated or filtered. The pH of the slurries was adjusted using HNO_3 or KOH. Slurry 7-1 included 1.0% by weight of the abrasive particles and had a pH of 4. Slurry 7-2 included 1.0% by weight of the abrasive particles and had a pH of 10. Slurry 7-3 included 0.5% by weight of the abrasive particles and had a pH of 4. And, Slurry 7-4 included 1.5% by weight of the abrasive particles and had a pH of 4.

[0051] The slurries were separately used to 6-inch blanket thermal oxide (TOX) and nitride (NIT) wafers using the same equipment and procedures used in Example 6. The polishing results are shown in Table 3 below:

TABLE 3

	Polish rate (nm/min)		Polish rate (nm/min)		Polish rate (nm/min)			Surface	TOX/NIT
Sample	TOX Used	WIWNU	TOX2 New	WIWNU	Avg TOX	NIT	WIWNU	Rough (nm)	Selectivity
7-1	15.9	28.18%	19.1	9.29%	17.5	148.45	1.73%	1.1–1.3	0.1178848
7-2	117.6	39.52%	92.6	11.78%	105.1	124.4	23.37%	1.3–1.4	0.8448553
7-3	179.6	11.95%	152.2	22.72%	165.9	114.6	20.37%	1.2–2.1	1.447644
7-4	37.7	22.79%	24.4	14.65%	31.05	197.75	34.92%	0.9–1.0	0.1570164

[0052] The basic pH value 1 0 may be a little closer to the IEP of hydrothermally created ceria particles (IEP=~8.5), resulting in a pronounced increase of secondary particle size after slurry formulation (Dmean=416 nm at pH=10 vs. 149 nm at pH=4), and thus higher oxide removal rate and rougher surface finish. It is somewhat surprising that an increase in TOX polishing rate was observed when the weight percent of abrasive particles at a pH of 4 was reduced from 1.0% (Slurry 7-1) to 0.5% (Slurry 7-3). It is possible that the relatively large secondary particles from Slurry 7-2 may have contaminated and been retained as residue on the polishing pad during the polishing with Slurry 7-3. It is also possible that the more dilute slurry (Slurry 7-3) provides more opportunities for the abrasive particles to contact the wafer and pad and thus results in a higher removal rate.

[0053] Additional advantages and modifications will readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to the specific details and illustrative examples shown and described herein. Accordingly, various modifications may be made without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.

What is claimed:

1. A method of producing abrasive particles for use in CMP slurries comprising:

    a. providing an aqueous reaction mixture comprising

        i. one or more compounds that provide a source of cerium ions,

        ii. one or more compounds that provide a source of metal ions selected from the group consisting of Be, B, Mg, Al, Si, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Ga, Ge, As, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Ba, La, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Hp, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, and combinations thereof,

    b. contacting the aqueous reaction mixture with a base to raise the pH to above about 1.5, and,

    c. subjecting the aqueous reaction mixture to hydrothermal treatment at a temperature of from about 70° C. to about 500° C. to produce the abrasive particles,

    d. wherein the abrasive particles comprise crystallites having crystal lattice structures that include cerium and one or more metals other than cerium.

2. The method of claim 1 wherein the ratio of cerium ions to guest ions is about 100000:1 to about 1:100000.

3. The method of claim 1 where the compound that provides the source of cerium ions is a Ce(III) salt or a Ce(IV) salt.

4. The method of claim 1 wherein the reaction mixture is subjected to hydrothermal treatment for about 10 minutes to about 48 hours.

5. The method of claim 4 wherein the aqueous reaction mixture is contacted with the base by double jet injection.

6. The method of claim 5 wherein the compound that provides the source of guest ions is a salt of the guest ion.

7. The method of claim 6 wherein the compound that provides the source of guest ions is selected from the group consisting of $Fe(NO_3)_3$, $Cu(NO_3)_2$, $Nd(NO_3)_3$, and hydrated forms thereof.

8. The method of claim 1 wherein the particles have a crystallite size of about 5 to about 100 nm.

9. The method of claim 1 wherein the particles agglomerate to form a secondary particle size of about 50 to about 500 nm.

10. A method of making composite CMP ceria particles comprising:

    a. contacting an aqueous solution of $Ce(NH_4)_2(NO_3)_6$ with a second metal salt to form a reaction mixture;

    b. contacting the reaction mixture with a base to raise the pH to above about 1.5; and

    c. heating the reaction mixture to form the particles.

11. The method of claim 10 wherein the second reaction mixture is heated for about 10 minutes to about 48 hours at a temperature of about 70° C. to about 500° C.

12. The method of claim 10 wherein the first reaction mixture is contacted with the base by double jet injection

13. The method of claim 10 wherein the second metal salt is selected from the group consisting of nitrates, chlorides, bromides, sulfates, perchlorides, and acetates of iron, copper and neodymium in their anhydrous and hydrated forms.

14. The method of claim 10 wherein the second metal salt is selected from the group consisting of $Fe(NO_3)_3$, $Cu(NO_3)_2$, $Nd(NO_3)_3$, and hydrated forms thereof.

15. A method of removing a film at a desired rate in the absence of chemical oxidizers comprising:

    a. determining the desired polishing rate of film to be removed;

    b. selecting abrasive particles according to claim 1 that provide a desired polishing rate for the film be removed; and

    c. polishing the film with a CMP slurry comprising the particles selected in step b.

16. The method of claim 15 wherein the film be removed is selected from the group consisting of silver, gold, platinum, copper, palladium, nickel, cobalt, iron, ruthenium, iridium, and osmium, silicon, aluminum, germanium, tungsten, tantalum, and alloys or blends thereof.

17. The method of claim 15 wherein the film to be removed is selected from the group consisting of oxides, nitrides or silicides of boron, sodium, magnesium, aluminum, silicon, phosphorus, potassium, calcium, gallium, germanium, arsenic, selenium, rubidium, strontium, yttrium, zirconium, tin, antimony, cesium, nickel, cobalt and barium.

18. The method of claim 15 wherein the film to be removed is a polymer is selected from the group consisting of poly(para-xylylenes), halogenated poly(para-xylylenes), b-staged polymers, polyimides, halogenated polyimides, silsequioxanes, alkyl substituted silsequioxanes, poly-(arylene ethers) and poly-(tetrafluoroethylene).

19. The method of claim 15 wherein the CMP slurry further comprises a pH adjuster.

20. A CMP slurry comprising:

    a. water; and

    b. abrasive particles according to claim 1.

21. The CMP slurry of claim 20 wherein the slurry is substantially free of chemical additives/oxidizers.

22. The CMP slurry of claim 20 wherein the ratio of cerium ions to guest ions is about 1000:1 to about 1:1000.

23. The CMP slurry of claim 21 wherein the guest ion is selected from the group consisting of Fe, Nd, and Cu.

24. The CMP slurry of claim 21 wherein the guest ion is selected from the group consisting of Ti, Ta and Y.

25. A method of removing a portion of a substrate in a CMP operation comprising:

a. providing the CMP slurry of claim 20;

b. adjusting the pH of the slurry to 3.0 to 11.0 using at least one pH adjuster;

c. contacting the slurry and the substrate to be polished; and

d. performing CMP on the substrate using said slurry.

26. The method of claim 25 wherein the difference in electronegativity of the cerium ions and the guest ions is sufficient to drive a redox reaction between the particle and the substrate when the particle contacts the substrate.

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